Ab initio study of the structure and relative stability of $MgSiO_4H_2$ polymorphs at high pressures and temperatures

Natalia V. Solomatova[1], Razvan Caracas[1,2], Luca Bindi[3,4], Paul D. Asimow[5]

[1]CNRS, Ecole Normale Supérieure de Lyon, Laboratoire de Géologie de Lyon LGLTPE UMR5276, Centre Blaise Pascal, 46 allée d'Italie Lyon 69364, France
[2]The Center for Earth Evolution and Dynamics (CEED), University of Oslo, Blindern, Oslo, Norway
[3]Dipartimento di Scienze della Terra, Università degli Studi di Firenze,Via G. La Pira 4, I-50121 Firenze, Italy
[4]C.N.R., Istituto di Geoscienze e Georisorse, Sezione di Firenze, Via G. La Pira 4, I-50121 Firenze, Italy
[5]Division of Geological & Planetary Sciences, Caltech, Pasadena, CA 91125 U.S.A.

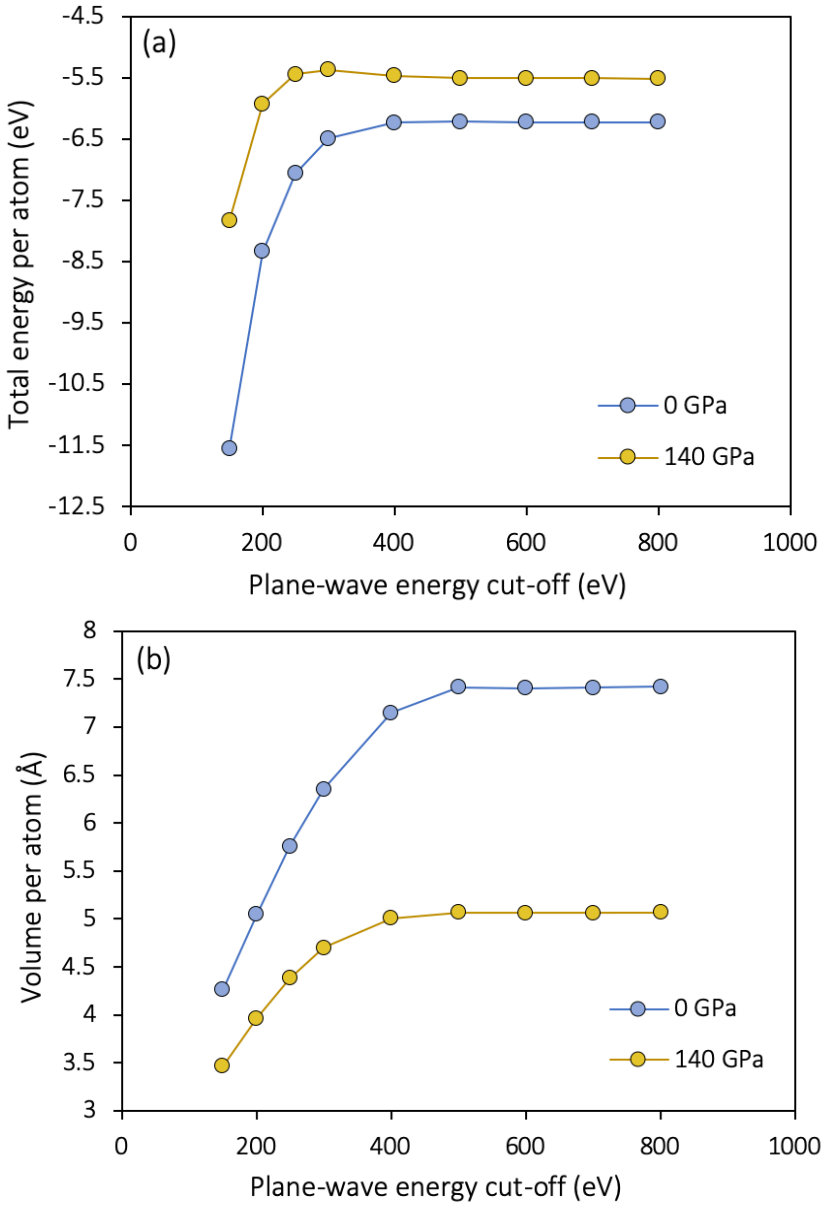

Figure 1. Convergence of the total energy and volume with respect to the plane-wave energy cut-off at 0 GPa (blue) and 140 GPa (yellow) for phase H. To ensure excellent convergence in volume and energy, a plane-wave energy cut-off of 600 eV was chosen, which results in an energy convergence of 2×10^{-3} eV/atom at 0 GPa and 6×10^{-4} eV/atom at 140 GPa and a volume convergence of 3×10^{-3} Å/atom at 0 GPa and 9×10^{-3} Å/atom at 140 GPa.

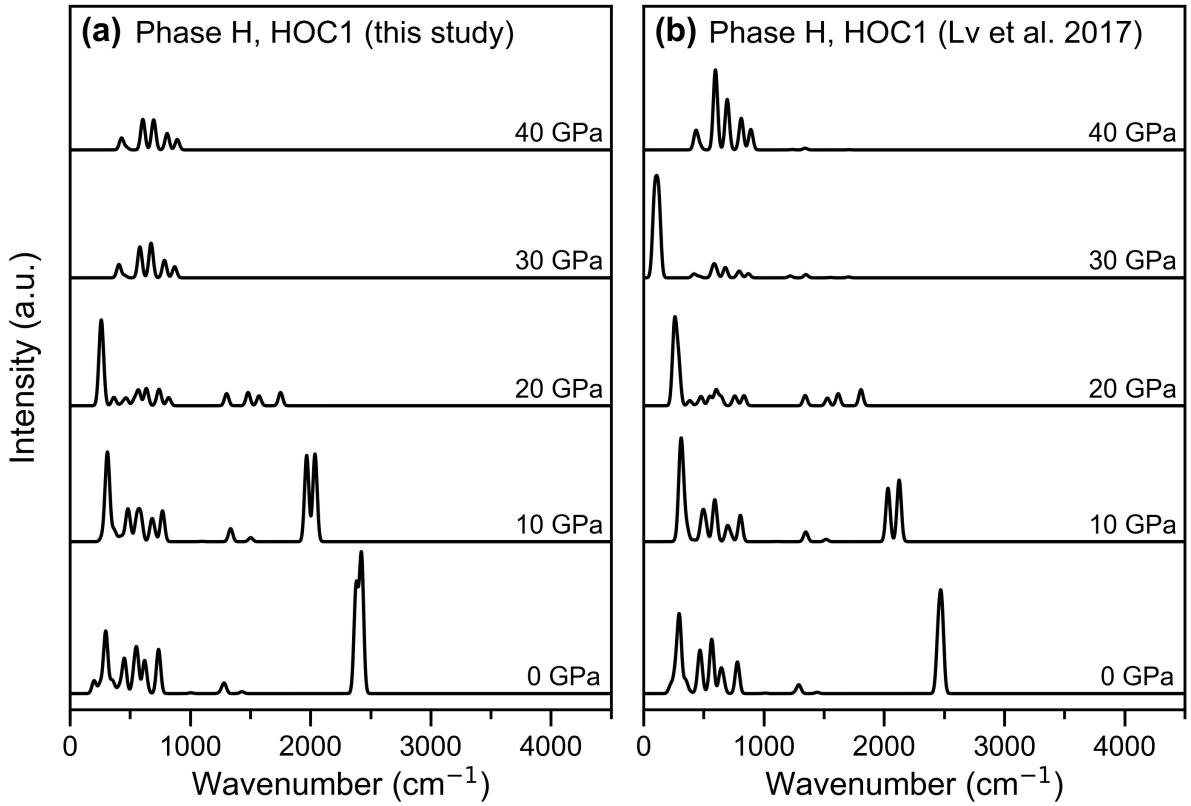

Figure 2. Raman spectra for phase H as a function of pressure, calculated using DFPT as implemented in ABINIT (this study) and CASTEP (Lv et al. 2017). O-H bond symmetrization is predicted at 30 GPa in this study while it is only observed at 40 GPa in the study of Lv et al. (2017), likely due to a difference in computational methods and bond distances. See Figure 7 of the main text for a comparison of the pressure-induced O-H bond symmetrization. When calculating the intensities, the wavelength of the laser source and temperature were set to 19636 cm^{-1} and 300 K, respectively.

Table 1. Lattice parameters and volume of phase H at ambient pressure from single crystal X-ray diffraction (Bindi et al. 2014) and from density functional theory calculations (this study; Tsuchiya 2013; Lv et al. 2017).

	a (Å)	b (Å)	c (Å)	γ (°)	V (Å^3)	Space group
Experiment (Bindi et al., 2014)	4.733(2)	4.3250(10)	2.8420(10)	90.0	58.18(3)	*Pnnm*
Theory (this study)	4.798	4.333	2.855	93.3	59.25	*Pm*
Theory (Tsuchiya 2013)	4.786	4.328	2.848	93.3	58.90	*Pm*
Theory (Lv et al. 2017)	4.812	4.349	2.863	93.3	59.84	*Pm*

Table 2. The distances and angles between oxygen and hydrogen in phase H at ambient pressure from single crystal X-ray diffraction (Bindi et al. 2014) and from density functional theory calculations (this study; Tsuchiya 2013; Lv et al. 2017). See Figure 7 of the main text for the pressure-induced changes in the O···O distance, O-H bond length and H-O-O bond angle.

	O-H (Å)	H···O (Å)	O···O (Å)	O-H-O (°)	Space group
Experiment (Bindi et al., 2014)	1.01	1.45	2.461(4)	178.9	*Pnnm*
Theory (this study)	1.04, 1.05	1.47, 1.54	2.51, 2.58	176.0, 178.3	*Pm*
Theory (Tsuchiya 2013)	1.08, 1.10	1.41, 1.45	2.49, 2.55	177.1, 179.0	*Pm*
Theory (Lv et al. 2017)	1.04, 1.04	1.49, 1.55	2.52, 2.59	175.7, 178.1	*Pm*

Table 3. Fitted Birch-Murnaghan parameters for phase H in the pressure range of about 35-60 GPa (after hydrogen bond symmetrization) with fixed K'_0 values of 4 and 5 for a direct comparison to the fits to experimental data by Nishi et al. (2018).

	V_0 (Å^3)	K_0 (GPa)	K'_0	Space group	P range (GPa)
Experiment (Nishi et al. 2018)	56.6(1)	204(2)	4 (fixed)	*Pnnm*	33.8-60.2
Theory (this study)	57.6(4)	193(1)	4 (fixed)	*P*2/*m*	35-60
Experiment (Nishi et al. 2018)	57.4(1)	167(2)	5 (fixed)	*Pnnm*	33.8-60.2
Theory (this study)	58.7(2)	155(1)	5 (fixed)	*P*2/*m*	35-60